

## PATENT SPECIFICATION

(11) 1323869

1323869

## NO DRAWINGS

(21) Application No. 50217/71 (22) Filed 28 Oct. 1971  
 (31) Convention Application No. 94698 (32) Filed 29 Oct. 1970  
 (31) Convention Application No. 5966 (32) Filed 13 Feb. 1971  
 (31) Convention Application No. 53730 (32) Filed 19 July 1971 in  
 (33) Japan (JA)  
 (44) Complete Specification published 18 July 1973  
 (51) International Classification C08G 47/02 G03C 1/68  
 (52) Index at acceptance  
 C3T 6D11 6D1A 6D1B 6D2A 6D5 6F1 6F2 6G10 6G2  
 6G3A 6G7F 6G8 6G9B 6J2D 6J2X 6J4  
 (72) Inventors MICHIHIRO OTO, TETSUYA MAYUZUMI,  
 TOJI FUJINO and ATSUMI NOSHIRO



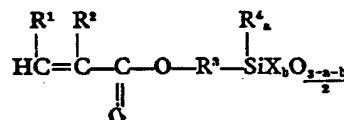
## (54) PHOTOPOLYMERIZABLE COMPOSITIONS

(71) We, DAI NIPPON PRINTING CO. LTD., of 12, Kaga-cho, 1-chome, Ichigaya, Shinjuku-ku, Tokyo, Japan, and SHINETSU CHEMICAL COMPANY, of 6-1 Otemachi 2-chome, Chiyoda-ku, Tokyo, Japan, both bodies corporate organised and existing under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns photopolymerizable compositions containing organopolysiloxanes.

A number of photopolymerizable compositions have already been developed and are used in printing for various purposes such as plate-making. Recently, efforts have been made to produce photopolymerizable compositions containing silicones as their main components, but, up to now, none of these compositions have exhibited satisfactory properties when put to practical uses, e.g., when used for plate-making in printing.

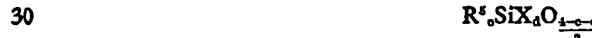
The photopolymerizable compositions of the invention comprise (1) at least one organopolysiloxane containing at least one photopolymerizable organic silicon unit of the general formula:



(I)

where  $\text{R}^1$  is a hydrogen atom or an unsubstituted or halogen-substituted phenyl radical,  $\text{R}^2$  is a hydrogen atom or a methyl radical,  $\text{R}^3$  is an unsubstituted or halogen-substituted bivalent  $\text{C}_{1-10}$  hydrocarbon radical optionally interrupted by an ether and/or ester linkage,  $\text{R}^4$  is an unsubstituted or halogen-substituted univalent  $\text{C}_{1-10}$  hydrocarbon radical,  $\text{X}$  is a hydroxy or  $\text{C}_{1-4}$  alkoxy radical, and  $a$  is 0 or 1, and  $b$  is 0, 1 or 2, with the proviso that  $(a+b)=0, 1$  or 2, (2) at least one photosensitizer and (3) a solvent for the components (1) and (2).

The organopolysiloxane must be an organic silicon compound. The or each photopolymerizable organic silicon unit present in the organopolysiloxane is bonded by a siloxane-bond ( $\equiv\text{Si}—\text{O}—\text{Si}\equiv$ ) to an organic silicon residue comprising at least one unit of the general formula:



5

10

15

20

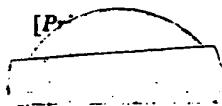
20

25

30

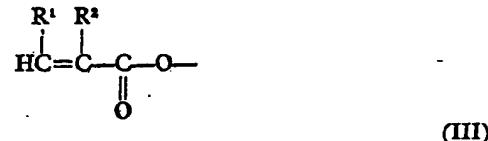
(II)

where  $\text{R}^5$  is an unsubstituted or halogen-substituted univalent  $\text{C}_{1-10}$  hydrocarbon radi-



cal, X is as defined above and each of c and d is 0, 1, 2 or 3, with the proviso that  $(c+d)=0, 1, 2$  or  $3$ . Organic silicon compounds comprising one or more units of the general formula (II) may be oily, rubbery or resinous in appearance, and straight-chained, branched chained, or cyclic in structure.

5. The photopolymerizability of the unit of formula (I) is due to the presence of the organic radical of the general formula:



(where  $R^1$  and  $R^2$  are as defined above). This organic radical is exemplified by acryloxy, methacryloxy, cinnamoyloxy and halogenocinnamoyloxy radicals.

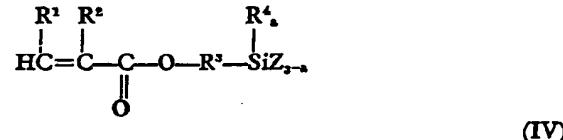
10 The radical represented by  $R^{\bullet}$  is exemplified by alkylene radicals such as methylene, trimethylene, tetramethylene and 2,2-dimethyl-trimethylene; arylene radicals such as phenylene; alkarylene radicals; and aralkylene radicals such as phenylethylene; and their halogen-substituted analogues; and alkylene radicals interrupted by ether and/or ester linkages, such as  $-\text{CH}_2\text{CH}_2-\text{OOCCH}_2\text{CH}_2-$ .

15  $\text{---CH}_2\text{CH}_2\text{---OOC---CH}_2\text{---}$ , and  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{CH}_2\text{---OOCCH---CH}_2\text{---}$

radicals, and their homologues in which the total number of carbon atoms does not exceed 10. The unsubstituted or halogen-substituted univalent  $C_{1-10}$  hydrocarbon radical represented by  $R^4$  or  $R^5$  is exemplified by alkenyl radicals such as vinyl and allyl; cycloalkenyl radicals such as cyclohexenyl; alkyl radicals such as methyl, ethyl, propyl and octyl; aryl radicals such as phenyl; aralkyl radicals such as benzyl and phenethyl; and alkaryl radicals such as styryl and tolyl and their halogen-substituted analogues such as chloromethyl, trichloroethyl, perfluorovinyl, trifluoropropyl and perchlorotolyl radicals.

25 The organopolysiloxane (component 1) can be prepared by known procedures represented generally by the two methods described below.

In one of these methods, a photopolymerizable organic silicon monomer of the general formula:

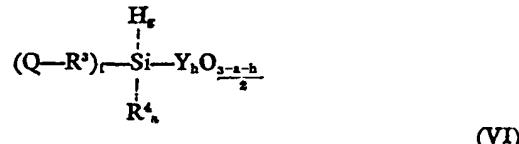


30 where  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $\alpha$  are as defined above, and  $Z$  is a halogen atom or an acetoxy, hydroxy or  $C_{1-4}$  alkoxy radical, is subjected to a condensation reaction with a silane or siloxane comprising at least one unit of the general formula:



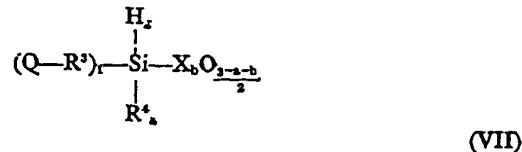
35 where  $R^5$  and  $c$  are as defined above,  $Y$  is a halogen atom or an acetoxy, hydroxy,  $NaO-$  or  $C_{1-4}$  alkoxy radical and  $e$  is 1, 2, 3 or 4 with the proviso that  $(c+e)$  is not greater than 4. This method is referred to hereinafter as the Monomer Method.

In the other of these methods, a silane or siloxane comprising at least one unit of the general formula:



5 where  $R^3$ ,  $R^4$ ,  $Y$  and  $a$  are as defined above,  $Q$  is a halogen atom or a hydroxy or  
epoxy group,  $h$  is 0, 1, 2 or 3, and each of  $f$  and  $g$  is 0 or 1 with the proviso that  
 $(f+g)=1$  and that  $(a+h)$  is not greater than 3, is subjected to a condensation reac-  
tion with a silane or siloxane comprising at least one unit of formula (V) above, to  
produce an organopolysiloxane containing at least one unit of the general formula:

5



10 where  $Q$ ,  $R^3$ ,  $R^4$ ,  $X$ ,  $a$ ,  $b$ ,  $f$ ,  $g$ ,  $(f+g)$  and  $(a+h)$  are as defined above, and the organo-  
polysiloxane thus obtained is then reacted with an organic compounds which contains  
10 a photopolymerizable organic radical of formula (III) above, and an aliphatic unsatura-  
ted bond in the case where  $f=0$ , or is an alkali metal or tertiary amine salt of a  
carboxylic acid containing a photopolymerizable organic radical of formula (III)  
above in the case where  $f=1$ . This method is referred to hereinafter as the Polymer  
Method.

10

15 The photopolymerizable organic silicon monomer of formula (IV) above used  
in the Monomer Method can be synthesized by various known methods. For example,  
it may be prepared by effecting an addition reaction between (i) a compound containing  
15 a photopolymerizable organic radical of formula (III) above and an aliphatic unsatura-  
ted bond, and (ii) a silane of the general formula:

15



20 where  $R^4$ ,  $Z$  and  $\alpha$  are as defined above, in the presence of a catalyst such as chloro-  
platinic acid, or by reacting (i) an alkali metal or tertiary amine salt of a carboxylic  
acid containing a photopolymerizable organic radical of formula (III) above with (ii)  
20 an organoalkoxy silane of the general formula:

20



25 where  $Q$ ,  $R^3$ ,  $R^4$  and  $a$  are as defined above, and  $R^6$  is a univalent  $C_{1-4}$  hydrocarbon  
radical.

25

Compounds containing a photopolymerizable organic radical of formula (III)  
above and an aliphatic unsaturated bond, which compounds may be used in the  
30 Polymer Method or in the preparation of the photopolymerizable organic silicon  
monomer of formula (IV) above, are exemplified by allyl esters derived from  
unsaturated carboxylic acids such as acrylic acid, methacrylic acid, cinnamic acid  
and halogen-substituted cinnamic acids, ethylene glycol diacrylate, ethylene glycol  
dimethacrylate, ethylene glycol dicinnamate, propylene glycol -diacrylate and -tri-  
35 methacrylate, neopentyl glycol dimethacrylate, trimethylmethane trimethacrylate, tri-  
methylpropane trimethacrylate and trimethylethane tricinnamate. Silanes represented  
by formula (VIII) above are exemplified by chlorosilanes such as trichlorosilane,  
30 methylchlorosilane, ethylchlorosilane, propylchlorosilane, isopropylchlorosilane,  
butylchlorosilane, hexylchlorosilane, octylchlorosilane, 2-ethylhexylchlorosilane,  
phenylchlorosilane, tolylchlorosilane, cyclohexylchlorosilane, chloro-  
40 methylchlorosilane,  $\gamma$ -bromopropylchlorosilane,  $\gamma$ -trifluoropropylchlorosilane,  
chlorophenylchlorosilane, trifluoromethylphenylchlorosilane, dimethylmonochloro-  
silane, methylethylmonochlorosilane, methylphenylmonochlorosilane, ethyltolymono-  
45 chlorosilane, methyltrifluoropropylmonochlorosilane, ethylcyclohexylmonochlorosilane  
and diphenylmonochlorosilane; and corresponding silanes in which a part or the whole  
of the chlorine atoms directly bonded to the silicon atoms are replaced by other  
halogen atoms or by acetoxy, hydroxy or  $C_{1-4}$  alkoxy radicals, e.g., trimethoxysilane,  
chlorodiethoxysilane, methyl dibutoxysilane, isopropyldiacetoxysilane, phenylmethyl-

30

35

40

45

silanol, ethyldibromosilane, ethoxydiacetoxysilane, dimethyliodidosilane, phenylisopropoxybromosilane, phenyldisilanol, cyclohexyldiacetoxysilane, tertiary butyldibromosilane, tolyldifluorosilane and tolylfluoropropylidethoxysilane.

Alkali metal and tertiary amine salts of carboxylic acids containing photopolymerizable organic radicals of formula (III) above are exemplified by the sodium, pyridium, potassium, dimethylaniline and triethylamine salts of acrylic acid, methacrylic acid, cinnamic acid and halogen-substituted cinnamic acids. Examples of organoalkoxysilanes represented by the general formula (IX) above are chloromethyltrimethoxysilane, bromomethyltrimethoxysilane, chloromethylmethyldimethoxysilane, iodomethylmethyldiethoxysilane, chloromethyltriisopropoxysilane,  $\beta$ -bromoethyltriethoxysilane,  $\beta$ -chloroethylmethyldimethoxysilane,  $\gamma$ -chloropropyltrimethoxysilane,  $\gamma$ -chloropropyltriethoxysilane,  $\gamma$ -bromopropylmethyldibutoxysilane,  $\gamma$ -iodopropylidisopropoxysilane,  $\gamma$ -bromoisobutylidiphenylethoxysilane,  $\delta$ -chlorobutyltrimethoxysilane,  $\beta$ -bromoethylphenyltriethoxysilane, chloromethylallyldimethoxysilane, chloromethylvinyltrimethoxysilane,  $\gamma$ -chloropropylvinylidethoxysilane,  $\gamma$ -bromopropylvinylphenylethoxysilane, and  $\delta$ -iodobutylallyldisopropoxysilane.

Photopolymerizable organic silicon monomers represented by the general formula (IV) above are exemplified by acryloxymethyltrichlorosilane,  $\gamma$ -methacryloxypropyltrichlorosilane,  $\delta$ -methacryloxybutyltriethoxysilane, and -trichlorosilane,  $\gamma$ -acryloxypropyl-methyldimethoxysilane, -methylidichlorosilane and -phenyldichlorosilane, methacryloxyethyl trihydroxysilane,  $\gamma$ -methacryloxypropylmonomethoxydichlorosilane, cinnamoyloxyethyltrichlorosilane, halogenocinnamamoiloxyethyltrimethoxysilane,  $\gamma$ -cinnamoyloxypropyl-trimethoxysilane and trichlorosilane,  $\delta$ -halogen-substituted cinnamoiloxybutyltrihydroxysilane, and trichlorosilane, and  $\gamma$ -methacryloxypropyltetra-

methoxydisiloxane. Further, silanes and siloxanes comprising one or more units of formula (V) above are exemplified by chlorosilanes such as tetrachlorosilane, methyltrichlorosilane, ethyltrichlorosilane, propyltrichlorosilane, 2-ethylhexyltrichlorosilane, vinyltrichlorosilane, allyltrichlorosilane, cyclohexyltrichlorosilane, phenyltrichlorosilane, benzyltrichlorosilane, styryltrichlorosilane, tolyltrichlorosilane, chloromethyltrichlorosilane,  $\gamma$ -trifluoropropyltrichlorosilane,  $\gamma$ -bromopropyltrichlorosilane, parachlorotolyltrichlorosilane, dimethylidichlorosilane, methylethyldichlorosilane, methylbutyldichlorosilane, methylcyclohexylidichlorosilane, methylphenylidichlorosilane, methylvinylidichlorosilane, methylallyldichlorosilane, methyltolyldichlorosilane,  $\gamma$ -trifluoropropylmethyldichlorosilane, chloromethylphenylidichlorosilane,  $\gamma$ -chloropropylphenylidichlorosilane, diphenyldichlorosilane, phenylvinylidichlorosilane, phenylcyclohexylidichlorosilane, trimethylchlorosilane, methylphenylchlorosilane, diethylphenylchlorosilane, triphenylchlorosilane, dimethylphenylchlorosilane, dimethylchloromethylchlorosilane,  $\gamma$ -trifluoropropylidemethylchlorosilane, dicyclohexylchlorophenylchlorosilane, ethylisobutyltolylchlorosilane and vinylethylphenylchlorosilane; by corresponding silanes in

which a part or the whole of the chlorine atoms directly bonded to silicon atoms are replaced by other halogen atoms, or by acetoxy, hydroxy or  $C_{1-4}$  alkoxy radicals; and by siloxanes obtained by subjecting these silanes to cohydrolysis, dehydrate, dehydrohalogenation, deacetylation, dealcoholization, dealkyl acetylation or dealkyl halogenation. Siloxanes comprising units of formula (V) above can be oily, rubbery, or resinous in appearance, and straight-chained, side-chained or cyclic in structure, so long as they contain at least one chlorine atom or acetoxy, hydroxy or  $C_{1-4}$  alkoxy radical directly bonded to a silicon atom. Furthermore, these siloxanes can be either of low molecular weight and contain several silicon atoms or of high molecular weight and contain hundreds or thousands of silicon atoms bonded together.

There are many ways in which the photopolymerizable organic silicon monomer of formula (IV) above can be condensed with the silane or siloxane comprising one or more units of formula (V) above to produce the organopolysiloxane (component 1). For example, a mixture of (a) the photopolymerizable organic silicon monomer of formula (IV) above and (b) the silane or siloxane comprising one or more units of formula (V) above may be cohydrolysed and then subjected to a dehydration or,

when both (a) the photopolymerizable organic silicon monomer of formula (IV) above and (b) the silane or siloxane comprising one or more units of formula (V) above possess silanol radicals, the starting materials may be mixed and then subjected to a dehydration, in which, in order to accelerate the reaction, it is preferable to use a known catalyst such as sulphuric acid, phosphoric acid, isopropyl ortho-titanate or sodium ethylate. In the case where one of (a) the photopolymerizable organic silicon monomer of formula (IV) above and (b) the silane or siloxane comprising one or more units of formula (V) above possesses a halogen atom or an acetoxy radical bonded to a silicon atom and the other possesses a silanol radical bonded to a silicon atom, the starting materials may be mixed and subjected to dehydrohalogenation or deacety-

lation, during which generated hydrogen halide or acetic acid should be either removed from the reaction system or inactivated by use of an acid acceptor. If one of (a) the photopolymerizable organic silicon monomer of formula (IV) above and (b) the silane or siloxane comprising one or more units of formula (V) above possesses an alkoxy radical bonded to a silicon atom, and the other possesses a silanol radical bonded to a silicon atom, the starting materials may be mixed and subjected to dealcoholization, during which generated alcohol should be removed from the reaction system. In order to accelerate the dealcoholization, it is preferable to use a known catalyst such as sulphuric acid, phosphoric acid, *para*toluenesulphonic acid, isopropyl titanate or sodium ethylate. In the case where one of (a) the photopolymerizable organic silicon monomer of formula (IV) above and (b) the silane or siloxane comprising one or more units of formula (V) above possesses an alkoxy radical bonded to a silicon atom, and the other possesses a halogen atom or an acetoxy radical bonded to a silicon atom, the starting materials may be mixed and subjected to dehaloalkylation or dealkylacetylation, in which, in order to accelerate the reaction, it is preferred to use a catalyst such as zinc chloride or ferric chloride, and during which generated alkyl halide or alkyl acetate should be removed from the reaction system. In each of the reactions mentioned above in which the photopolymerisable organic silicon monomer of formula (IV) above is condensed with the silane or siloxane comprising one or more units of formula (V) above, it is preferred to use a suitable amount of an organic solvent to enable the reaction to be carried out easily. Examples of solvents that may be used are methyl ethyl ketone, methyl isobutyl ketone, benzene, toluene, and xylene. In order to accelerate these reactions, it is sometimes desirable to raise the temperature of the reaction system. In such a case, it is preferable to add a thermal polymerization inhibitor, such as a quinone, e.g., hydroquinone or benzoquinone, an amine salt or a hydrazine salt, in order to protect the organic radical of formula (III) contained in the photopolymerizable organic silicon monomer of formula (IV). The first step of the Polymer Method may be effected by procedures similar to those used in practising the Monomer Method. For example, a mixture of (a) the silane or siloxane comprising one or more units of formula (VI) above with (b) the silane or siloxane comprising one or more units of formula (V) above may be subjected to cohydrolysis, dehydration, dehydrohalogenation, deacetylation, dealcoholization, dealkyl acetylation or dehaloalkylation, depending upon the radical Y contained in the silane or siloxane comprising one or more units of formula (V). The reaction conditions and any catalyst used may be selected as in the Monomer Method. Examples of silanes and siloxanes comprising one or more units of formula (VI) above are chlorosilanes such as trichlorosilane, methyl dichlorosilane, ethyl dichlorosilane, propyl dichlorosilane, isopropyl dichlorosilane, butyl dichlorosilane, hexyl dichlorosilane, octyl dichlorosilane, 2-ethylhexyl dichlorosilane, phenyl dichlorosilane, tolyl dichlorosilane, cyclohexyl dichlorosilane, chloromethyl dichlorosilane,  $\gamma$ -bromo-propyl dichlorosilane,  $\gamma$ -trifluoropropyl dichlorosilane, chlorophenyl dichlorosilane, trifluoromethylphenyl dichlorosilane, dimethyl monochlorosilane, methyl ethyl monochlorosilane, methyl phenyl monochlorosilane, ethyl tolyl monochlorosilane, methyl trifluoro-propyl monochlorosilane, ethyl cyclohexyl monochlorosilane, diphenyl monochlorosilane, chloromethyl trichlorosilane, bromomethyl trichlorosilane, iodomethyl trichlorosilane,  $\beta$ -bromoethyl trichlorosilane,  $\beta$ -chloroethyl trichlorosilane,  $\gamma$ -chloropropyl trichlorosilane,  $\gamma$ -bromopropyl trichlorosilane,  $\gamma$ -iodopropyl trichlorosilane,  $\gamma$ -bromo isobutyl trichlorosilane,  $\delta$ -chlorobutyl trichlorosilane,  $\beta$ -bromoethylphenyl trichlorosilane, chloromethyl dichlorosilane, bromomethyl tolyl dichlorosilane, bromomethylphenyl dichlorosilane,  $\delta$ -iodobutylphenyl dichlorosilane,  $\gamma$ -chloropropyl dimethyl chlorosilane, and chlorophenyl trichlorosilane; corresponding silanes in which a part or the whole of the chlorine atoms directly bonded to the silicon atoms are replaced by other halogen atoms or by acetoxy, hydroxy or  $C_{1-4}$  alkoxy radicals; and siloxanes prepared by subjecting said silanes obtained by substitution to cohydrolysis, dehydration, dehydrohalogenation, deacetylation, dealcoholization, dealkylacetylation or dehaloalkylation. Siloxanes comprising units of formula (VI) above may be oily, rubbery or resinous in appearance and straight-chain, side-chained or cyclic in structure. Furthermore, these siloxanes can be either of low-molecular weight and contain several silicon atoms or of high-molecular weight and contain hundreds or thousands of silicon atoms bonded together so long as they contain at least one halogen atom or acetoxy, hydroxy, or  $C_{1-4}$  alkoxy radical bonded to a silicon atom. The other compounds used in the Polymer Method are exemplified above. The second step of the Polymer Method may be conducted by subjecting a mixture of the organopolysiloxane containing at least one unit of formula (VII) above and the said organic compound containing a photopolymerizable organic radical of

formula (III) above to either (a) a reaction to eliminate a halide salt, the starting materials being dissolved in dimethylformamide or in any other ether, or, preferably the reaction being conducted in the presence of a catalyst, such as a tertiary amine or pyridine, or (b) an addition reaction in the presence of chloroplatinic acid. Any substance that absorbs rays, and thus becomes excited and capable of giving energy to the organopolysiloxane (component 1) and accelerating the rate at which photopolymerization of that organopolysiloxane occurs, may be used in the present invention as a photosensitizer. Examples of photosensitizers that may be used are amino-, nitro- and phenol compounds, e.g., *p*-nitrodiphenyl, *p*-nitroaniline, 5-nitroacenaphthene, picramide, 2,6 - dichloro - 4 - nitroaniline and 2,4-dinitrophenol; ketone compounds, e.g., benzaldehyde, acetophenone, *p,p'*-diamino-benzophenone, and 4,4'-bis(dimethylamino)benzophenone (Michler's ketone); quinone compounds, e.g., benzoquinone, anthraquinone, and 1,2-naphthoquinone; anthrone compounds, e.g., 3-methyl-1,3-diazo-1,9-benzanthrone; dyes, e.g., malachite green, methylene blue, chrome green, rhodamine blue, and azo green TEC; and pyrilium salts, e.g., 2,4,6-triphenyl-pyrilium-perchlorate, 2,4,6-triphenyl-thiapyrilium-perchlorate, 2,4,6 - triphenyl - pyrilium-fluoborate, and 2,4,6 - triphenyl - thiapyrilium - fluoborate. The photosensitizer may be used in an amount of from 0.05 to 5.0 parts by weight with respect to the weight of the organopolysiloxane (component 1).

The photopolymerizable composition of the present invention contains a solvent so that the components (1) and (2) are dissolved and their viscosities can be controlled when the composition is coated over a substratum. Said solvent may be a ketone such as methyl-ethyl-ketone or methyl-isobutyl-ketone or an aromatic hydrocarbon such as benzene, toluene or xylene.

The compositions of the invention may also comprise a diluent such as a hydrocarbon halide, an alcohol, or an ester, in addition to the above mentioned solvent. It is not necessary that the components (1) and (2) should be soluble in the diluent. It is essential only that the diluent should be inert with respect to the organopolysiloxane (component 1). As opposed to the solvent, which is required to dissolve the components (1) and (2), the sole purpose of the diluent is to make the composition more suitable for particular applications. Moreover, the compositions of the invention may comprise any of the thermal polymerization inhibitors and fillers mentioned above in connection with known photopolymerizable compositions. Any appropriate amount of these additives may be used, but, since thermal polymerization inhibitors are intended to improve the stability during storage (prevention of reaction in the dark) of the compositions and prevent thermal polymerization from taking place, when the solvent has evaporated from the positions after they have been coated over substrata, it is preferred that about 0.05% by weight of polymerization inhibitor should be used with respect to the weight of the organopolysiloxane (component 1). When coated over some substrata and dried and exposed to ultra-violet or strong visible rays, photopolymerizable compositions in accordance with the invention give extremely strong and insoluble films, having superior heat-, chemical-, and corrosion-resistance. Any part of these compositions that is not exposed to rays can be easily washed away with a solvent, so that any picture can be formed from these compositions without difficulty. The exact mechanism by which the exposed part forms a film and the unexposed part is washed away with a solvent is not known, but, presumably, when these photopolymerizable compositions are coated over substrata, dried and exposed to rays, those photopolymerizable organic radicals of formula (III) above contained in the organopolysiloxane (component 1) that are exposed to the rays become excited by the rays, and by any photosensitizer or additive contained in these photopolymerizable compositions, and thus become polymerized, thereby forming a hard and insoluble film whereas those photopolymerizable organic radicals of formula (III) above and contained in the organopolysiloxane (component 1) that are not exposed to the rays remain unchanged by the rays and are therefore easily washed away by the solvent.

Photopolymerizable compositions of the invention can be coated on substrata such as metal plates e.g. copper plates, aluminium plates, zinc plates, nickel plates, iron plates, and stainless plates; glass plates, and synthetic resin plates. The coatings can be formed by known methods, e.g. by flow, dip, whirler, spinner, spray or roller coating. Preferably, the light source to which the photopolymerizable composition is exposed is a lamp giving off rays rich in ultra-violet rays, such as a xenon lamp, or a low-pressure, medium-pressure, or high-pressure mercury arc lamp.

To produce a positive picture with the photopolymerizable composition on a substratum a positive film is closely applied to a thin layer of the photopolymerizable composition coated over the substratum, under reduced pressure, and exposed to

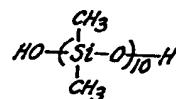
light. Then the layer of photopolymerizable composition is developed, dried and cured with heat; a film is formed in the part of the composition exposed to the rays. Films obtained in this manner have superior heat-, solvent-, and corrosion-resistance and can therefore be very advantageously put to various uses such as plate-making in printing, or resists for etching in printed circuit making. Furthermore, films obtained in this manner have very little spattering and can therefore be used as resists for ion-etching.

When the organopolysiloxane (component 1) is prepared by reacting methylpolysiloxane with an unsaturated compound of formula (IV) above, it can be used to prepare a planographic printing plate, by photopolymerizing the methylpolysiloxane in the ground part to produce a film, having superior releasability and a critical surface tension of about 21 dyn/cm. By using this method the dampening solution hitherto required in the preparation of a planographic printing plate can be dispensed with. When this organopolysiloxane is used as a resist in forming a metal pattern by a continuous plating method, the resulting metal pattern can be easily released by use of an adhesive.

The following Examples, in which all parts are by weight, illustrate the invention.

Example 1

Into a four-necked flask, equipped with a stirrer and a cooling device, were introduced 152 parts of a straight-chained dihydroxydimethylpolysiloxane, having an average molecular weight of 758 and the general formula:



496 parts of  $\gamma$ -methacryloxypropyl trimethoxysilane, and 0.2 part of potassium acetate, and the resulting mixture was stirred at 80°C in a stream of nitrogen, while generated methanol was removed by an ester adapter equipped with a cooling device. When the distillation of methanol ceased, the reaction product was cooled and potassium acetate was filtered off to obtain a pale yellow transparent photopolymerizable siloxane. This siloxane, obtained in a 96% yield (188 parts), proved to have a viscosity of 13 cs (25°C).

A photosensitizer was added to this siloxane to give the following composition:

Photopolymerizable organopolysiloxane prepared in the manner described above:

4,4'-bis(dimethylamino)benzophenone	100 parts
Toluene	4 parts
	50 parts

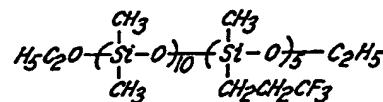
After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

When, picramide, 5-nitroacenaphthene, methylene blue, or 2,4,6-triphenylpyrilium perchlorate was used in place of the 4,4'-bis(dimethylamino)benzophenone, a similar result was obtained in each case.

Example 2

Into a four-necked flask were introduced 2500 parts of water, 500 parts of toluene and 50 parts of isopropyl alcohol, and the resulting mixture was cooled and kept at 5-10°C. A mixture of 74.8 parts of monomethyltrichlorosilane, 64.5 parts of dimethyl-dichlorosilane, 126.5 parts of diphenyldichlorosilane, 105.7 parts of mono-phenyltrichlorosilane, and 131 parts of  $\gamma$ -methacryloxypropyl trichlorosilane was added dropwise over one hour and then the resulting mixture was stirred for 30 minutes, and washed with water until its pH became 7.0. Subsequently, this mixture was distilled under reduced pressure until its siloxane concentration reached 50%. There was thus obtained a siloxane containing 3.0% of hydroxyl radicals. To this siloxane

were added 797 parts of diethoxy- $\gamma$ -trifluoropropylmethylpolysiloxane, having an average molecular weight of 1594, and the general formula:



5 1.0 part of paratoluenesulphonic acid, and 0.3 part of methoxyhydroquinone, as a polymerization inhibitor, and the resulting mixture was stirred at 110°C for 8 hours, while distilled ethanol was removed by means of a distillation column with which the flask was equipped. After the reaction was over, 10 parts of sodium carbonate was added to the reaction product and neutralization was allowed to occur at 80°C for 2 hours. The neutralized product was cooled. Paratoluenesulphonic acid and surplus sodium carbonate were distilled off, and toluene was removed by distillation under reduced pressure to obtain a solid pale yellow transparent silicone compound having a pour point of 43°C, in a 96% yield (1174 parts).

10 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

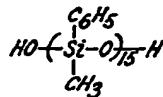
15 Photopolymerizable silicone prepared in the manner described above: 15  
 5-nitroacenaphthene 4 parts  
 Toluene 1000 parts

20 After this composition had been well stirred, it was spread by means of a spinner into a 10  $\mu$  thick layer over an aluminum plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C, to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

25 When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyrrolium perchlorate was used in place of the 5-nitroacenaphthene, a similar result was obtained in each case.

### Example 3

30 Into a four-necked flask were introduced 412 parts of a straight-chained dihydroxymethylphenylpolysiloxane, having an average molecular weight of 2058, and the general formula:— 30



35 412 parts of toluene, and 18.6 parts of pyridine, and while the resulting mixture was stirred at room temperature, 24.2 parts of  $\gamma$ -methacryloxypropylmethyldichlorosilane was added to it dropwise. The resulting mixture was then heated to 60°C, stirred for one hour, and then cooled. A white precipitate (pyridine hydrochloride) was obtained and was filtered off, and toluene was removed by distillation under reduced pressure, to obtain a pale yellow transparent photopolymerizable silicone compound having a viscosity of 135 cs (25°C), in a yield of 95% (409 parts). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

40 Photopolymerizable organopolysiloxane prepared in the manner described above: 40  
 45  $p$ -nitrodiphenyl 100 parts  
 Toluene 4 parts  
 50 parts 45

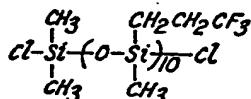
After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyrilium perchlorate was used in place of the *p*-nitrodiphenyl, a similar result was obtained in each case.

10

## Example 4

To 329 parts of the siloxane (50% toluene solution) used as a starting material in Example 2 were added 845 parts of dichloro- $\gamma$ -trifluoropropylmethylpolysiloxane, having an average molecular weight of 1689 and the general formula:



15

80 parts of pyridine and 329 parts of tetrahydrofuran, and the resulting mixture was stirred at 80-85°C for 4 hours. The reaction product was then washed with water in order to remove pyridine hydrochloride and tetrahydrofuran, and subjected to distillation under reduced pressure to remove toluene. A solid pale yellow, transparent photopolymerizable silicone compound, having a pour point of 35°C was thus obtained in a yield of 94% (1069 parts).

20

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

25

Photopolymerizable silicone prepared in the manner described above:

100 parts
4 parts
1000 parts

*p*-nitroaniline  
Toluene

15

After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

30

When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyrilium perchlorate was used in place of the *p*-nitroaniline, a similar result was obtained in each case.

35

## Example 5

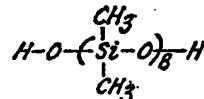
A mixture of 248 parts of  $\gamma$ -methacryloxypropyltrimethoxsilane and 464 parts of  $\gamma$ -methacryloxypropylmethyldimethoxsilane was added, dropwise over one hour, to a mixture of 712 parts of toluene, 50 parts of isopropylalcohol and 10 parts of acetic acid, placed in a four-necked flask, kept at 5-10°C. The resulting mixture was stirred for 2 hours, and then washed with water until it became neutral. The reaction product thus obtained was subjected to distillation under reduced pressure in order to remove toluene, and to the resulting product (concentration of silicone compound: 60%) were added 610 parts of dihydroxydimethylpolysiloxane, having an average molecular weight of 610 and the general formula:

30

35

40

45



0.3 part of tin octoate, and 0.2 part of methoxyhydroquinone, as a polymerization inhibitor. The resulting mixture was stirred at 100-110°C, while generated water

was removed, as an azeotropic mixture with toluene. When no more water was generated, toluene was removed by distillation under reduced pressure to obtain a colourless, transparent liquid photopolymerizable silicone compound in a 93% yield (1105 parts).

5 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

5

Photopolymerizable silicone prepared in the manner described above:

Picramide	100 parts
Toluene	4 parts
	50 parts

10 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

10

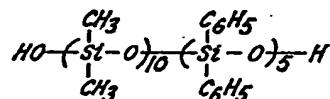
15 When methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the picramide, a similar result was obtained in each case.

15

Example 6

20 Into a four-necked flask were introduced 175 parts of a straight-chained dihydroxymethylphenylsiloxane, having an average molecular weight of 1748, and the general formula:

20



25 36 parts of  $\gamma$ -cinnamoxypropyltriacetoxysilane and 175 parts of toluene, and the resulting mixture was heated to 75-80°C. After the mixture had been stirred for 30 minutes, 5.4 parts of water was added to it, and the mixture was then stirred for a further 4 hours. The resulting reaction product was then distilled under reduced pressure to remove acetic acid and toluene and obtain a pale yellow transparent photopolymerizable silicone compound in a 95% yield (188 parts). The viscosity of this silicone compound proved to be 153 cs (25°C). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

25

30 35 Photopolymerizable organopolysiloxane prepared by the above-given method:

2,6-dichloro-4-nitroaniline	100 parts
Toluene	4 parts
	50 parts

30

35 After the composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

40

40 When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the 2,6-dichloro-4-nitroaniline, a similar result was obtained in each case.

40

45 50 Example 7

500 parts of water, 74 parts of toluene, and 99 parts of n-butyl alcohol were placed in a four-necked flask and cooled to 10°C or under. A mixture of 74 parts of dimethyldichlorosilane, 101 parts of diphenyldichlorosilane, 21 parts of monophenyltrichlorosilane, and 29 parts of  $\gamma$ -methacryloxypropyltriethoxysilane was added dropwise over one hour. The resulting mixture was stirred for 30 more minutes, and then allowed to stand so a layer of hydrochloric acid could separate. The solvent layer was

45

50

washed with water until its pH became 7-8, and then distilled under reduced pressure to remove toluene, butyl alcohol and generated water. A pale yellow, transparent photopolymerizable silicone compound having a four point of 73°C was thus obtained in a yield of 93% (160 parts). A photosensitizer and a solvent were added to the silicone compound to give the following composition:

5 Photopolymerizable organopolysiloxane obtained  
in the manner described above:

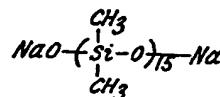
2,4-dinitrophenol	100 parts
Toluene	4 parts
	1000 parts

10 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

15 When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the 2,4-dinitrophenol, a similar result was obtained in each case.

20 Example 8

20 In a four-necked flask were placed 117 parts of a straight-chained disodium-dimethyl siliconate, having an average molecular weight of 1172 and the general formula:



25 and 59 parts of toluene. While the resulting mixture was stirred at room temperature, 33 parts of  $\gamma$ -cinnamoyloxypropylmethyldichlorosilane was added dropwise over 30 minutes. The resulting mixture was then stirred for a further 4 hours. Subsequently, generated sodium chloride was filtered off, and toluene was removed by distillation under reduced pressure to obtain, in a 95% yield, a colourless transparent photopolymerizable silicone compound (132 parts) whose viscosity proved to be 85 cs (25°C).

30 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

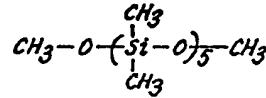
35 Photopolymerizable organopolysiloxane prepared  
in the manner described above:

Benzaldehyde	100 parts
Toluene	4 parts
	50 parts

40 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed under reduced pressure to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance. When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the benzaldehyde, a similar results was obtained in each case.

45 Example 9

45 208 parts of a straight-chained dimethoxydimethylpolysiloxane, having an average molecular weight of 416, and the general formula:



48 parts of  $\gamma$ -methacryloxypropylmethyldichlorosilane, 0.3 part of ferric chloride, and 0.1 part of hydroquinone were placed in a four-necked flask, and the resulting mixture was slowly stirred while it was heated and attention was paid to the generation of methyl chloride so that the mixture was reacted at 75-85°C for one hour and at 110°C for three hours. When the generation of methyl chloride ceased, the reaction product was cooled, and, by use of activated charcoal, ferric chloride was filtered off. A colourless transparent photopolymerizable silicone compound having a viscosity of 10.3 cs (25°C) was thus obtained in a yield of 96% (197 parts).

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

Photopolymerizable organopolysiloxane prepared  
in the manner described above:

Acetophenone	100 parts
Toluene	4 parts
	50 parts

15 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed under reduced pressure to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion resistance.

20 When picramide, methyl blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the acetophenone, a similar result was obtained in each case.

Example 10

25 149 parts of monomethyltrichlorosilane, 247 parts of  $\gamma$ -acryloxypropyltrichlorosilane, and 0.1 part of hydroquinone were placed in a four-necked flask, and 128 parts of methanol were added dropwise at a temperature not exceeding 10°C. The resulting mixture was gradually heated to 120°C, while attention was paid to the generation of hydrochloric acid, and kept at this temperature for one hour. When no more hydrochloric acid was generated, the temperature was lowered to 50°C, 0.5 part of ferric chloride was added to the reaction product, and, while attention was paid to the generation of methyl chloride, the resulting mixture was heated to 130°C, and kept at that temperature for 4 hours. When no more methyl chloride was generated, the mixture was cooled to 50°C, 30 parts of methanol and 5 parts of sodium carbonate were added and the mixture was left to neutralize for one hour. Subsequently, generated sodium chloride and surplus sodium carbonate were filtered off, and the unreacted methanol was removed by distillation under reduced pressure, to obtain a colourless transparent liquid photopolymerizable silicone compound in a 90% yield (288 parts) and having a viscosity of 57 cs (25°C). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

Photopolymerizable organopolysiloxane prepared  
in the manner described above:

<i>p,p'</i> -diaminobenzophenone	100 parts
Toluene	4 parts
	50 parts

45 After the composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance. When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the *p,p'*-diaminobenzophenone, a similar result was obtained in each case.

Example 11

55 248 parts of  $\gamma$ -acryloxypropyltriethoxysilane, 740 parts of octamethylcyclotetrasiloxane, 0.25 part of methoxyhydroquinone as a polymerization inhibitor, and 50 parts of activated clay were placed in a three-necked flask, and the resulting mixture was reacted by stirring at 100°C for 8 hours. After the reaction was over, the acid clay was removed by filtration, and the unreacted substances were removed by distillation under reduced pressure to obtain a colourless transparent liquid photopolymeriz-

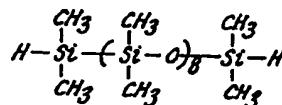
able silicone compound, whose viscosity was 110 cs (25°C), in a 96% yield (948 parts).

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

5	Photopolymerizable organopolysiloxane prepared in the manner described above:	5
	Benzoquinone	100 parts
	Toluene	4 parts
		1000 parts
10	After this composition had been well stirred, it was spread by means of a spinner, into a 10 $\mu$ thick layer over an aluminium plate and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3—4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C, to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.	10
15	When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the benzoquinone, a similar result was obtained in each case.	15

Example 12

368 parts of dimethylpolysiloxane, terminated with monohydrogendimethylsilyl radical, and having an average molecular weight of 726, and the general formula:



and 0.5 part of hydroquinone were placed in a three-necked flask, and kept at 75—85°C. Subsequently a mixture of 138 parts of allyl methacrylate and 0.2 part of chloroplatinic acid was added dropwise while attention was paid to the generation of heat. The reaction system was then further heated and allowed to react at 110°C for 8 hours. When the reaction ceased, unreacted allyl methacrylate was removed by distillation under reduced pressure to obtain a pale yellow transparent liquid photopolymerizable silicone compound having a viscosity of 150 cs (25°C) in a yield of 96% (474 parts).

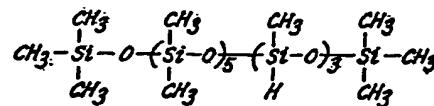
A photosensitizer and a solvent were added to this silicone compound to give the following composition:

25	Photopolymerizable silicone prepared in the manner described above:	25
	Anthraquinone	100 parts
30	Toluene	4 parts

After this composition had been well stirred, it was spread by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed to rays from a super-high pressure mercury arc lamp, placed 40 cm away, for 1—2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical- and corrosion-resistance.

When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the anthraquinone, a similar result was obtained in each case.

45	Example 13	45
	304 parts of allyl cinnamate, 0.2 part of a 2% isopropylalcohol solution of chloroplatinic acid and 0.3 part of methoxyhydroquinone were placed in a three-necked flask, stirred and heated to 80°C. 356 parts of hydromethylpolysiloxane terminated with trimethylsilyl radical and having an average molecular weight of 712 and the general formula:	
50		50



5 was added dropwise over one hour while attention was paid to the generation of heat. Subsequently, the reaction system was reacted at 100—105°C for four more hours to obtain a pale yellow transparent liquid photopolymerizable silicone compound having a viscosity of 40 cs (25°C) in a 98% yield (625 parts). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

	Photopolymerizable silicone prepared in the manner described above:	100 parts	
10	1,2-naphthoquinone	4 parts	
	Toluene	60 parts	10

15 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3—4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

15 When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the 1,2-naphthoquinone, a similar result was obtained in each case.

20 Example 14  
20 712 parts of the siloxane used as starting material in Example 12, 0.5 part of a 2% isopropylalcohol solution of chloroplatinic acid, 1500 parts of isopropylalcohol, 0.25 part of potassium acetate, and 0.5 part of hydroquinone were placed in a three-necked flask, and while the resulting mixture was kept at 78°C, 642 parts of diethyleneglycol dimethacrylate was added dropwise over one hour. Subsequently, the resulting mixture was kept at 78°C for another 8 hours to allow it to react. When the reaction ceased, isopropylalcohol and unreacted diethyleneglycol dimethacrylate were distilled off under reduced pressure, and then the reaction product was cooled. Potassium acetate was then removed by filtration to obtain a colourless transparent liquid photopolymerizable silicone compound having a viscosity of 105 cs (25°C) in a 93% yield (1259 parts).

25 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

35	Photopolymerizable silicone obtained in the manner described above:	100 parts	35
	3-methyl-1,3-diazo-1,9-benzanthrone	4 parts	
	Toluene	1100 parts	

40 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1—2 minutes. The layer was then developed with methyl ethyl ketone, dried and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

45 When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyridinium perchlorate was used in place of the 3-methyl-1,3-diazo-1,9-benzanthrone, a similar result was obtained in each case.

Example 15  
50 A mixture of 645 parts of dimethylchlorosilane, 300 parts of monomethyltrichlorosilane, and 115 parts of monomethylhydrogendichlorosilane was added dropwise over two hours to a mixture of 1000 parts of toluene, 300 parts of *n*-butanol and 5000 parts of water, kept at a temperature not exceeding 10°C. The resulting mixture was stirred for a further three hours, and was then washed with water until its pH became 6.8. Subsequently, toluene was removed from the reaction system by distilla-

tion under reduced pressure until the siloxane concentration in the system reached 50%, 0.5 part of a 2% octanol solution of chloroplatinic acid, 0.5 part of hydroquinone and 190 parts of allyl cinnamate were added to the reaction system, and, while attention was paid to the generation of heat, the resulting mixture was slowly heated to and then kept at 110°C for 10 hours. After reaction ceased, toluene and unreacted substances were removed by distillation under reduced pressure to obtain a pale yellow, transparent, liquid photopolymerizable silicone compound having a viscosity of 805 cs (25°C) in a 95% yield (714 parts).

5 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

5

Photopolymerizable organopolysiloxane prepared in the manner described above:	100 parts
Rhodamine blue	50 parts
Toluene	100 parts

10 After this composition had been well stirred, it was spread, by means of a spinner into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance. When picramide, 5-nitroacenaphthene, 4,4'-bis(dimethylamino)benzophenone or 2,4,6-triphenylpyriliun perchlorate was used in place of the rhodamine blue, a similar result was obtained in each case.

10

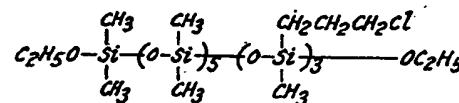
15

20

20

15 Example 16  
25 185 parts of  $\gamma$ -chloropropylmethylpolysiloxane, terminated with dimethylethoxy-silyl radical and having an average molecular weight of 927, and the general formula:

25



30 0.5 part of hydrofuran, 94 parts of dimethylformaldehyde, and 21 parts of triethylamine were placed in a three-necked flask. 69.8 parts of sodium methacrylate were added to the resulting mixture with stirring, and then the reaction system was stirred for two hours, heated to 80°C, and stirred for 4 more hours. When reaction ceased, the reaction product was cooled, unreacted sodium methacrylate and generated sodium chloride were removed by filtration, and dimethylformaldehyde was removed by distillation under reduced pressure to obtain a pale yellow, transparent, liquid photopolymerizable silicone compound having a viscosity of 30 cs (25°C), in a 95% yield (203 parts).

30

35 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

35

40 Photopolymerizable organopolysiloxane prepared  
in the manner described above:

100 parts	
Methylene blue	4 parts
n-propyl alcohol	50 parts
Toluene	50 parts

40

45 After this composition had been well stirred, it was spread by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

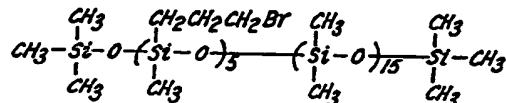
45

50 When picramide, 5-nitroacenaphthene, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the methylene blue, a similar result was obtained in each case.

50

**Example 17**

348 parts of  $\gamma$ -bromopropylmethylpolysiloxane, terminated with trimethylsilyl radical, and having an average molecular weight of 1394 and the general formula:



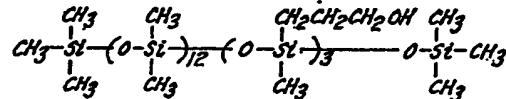
5        0.5 part of hydroquinone, 174 parts of tetrahydrofuran, and 17 parts of pyridine were placed in a three-necked flask, heated to 80°C, and 234 parts of sodium cinnamate was added with stirring. The resulting mixture was allowed to react at 80°C for 8 more hours. When the reaction ceased, the reaction system was cooled, unreacted sodium cinnamate and generated sodium chloride were removed by filtration, and tetrahydrofuran was removed by distillation to obtain a pale yellow, transparent, liquid photopolymerizable silicone compound having a viscosity of 380 cs (25°C), in a 96% yield (464 parts).

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

15	Photopolymerizable organopolysiloxane prepared in the manner described above:	100 parts	15
	Chrome green	4 parts	
	n-propyl alcohol	50 parts	
	Toluene	100 parts	
20	After this composition had been well stirred, it was spread by means of a spinner, into a $10 \mu$ thick layer over an aluminium plate, and was then exposed to rays from a super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at $150^{\circ}\text{C}$ to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.	20	
25	When a mixture of 5 micromoles of 4,4'-bis(trimethylsilyl)-1,10-phenanthrene, 100	25	

### Example - 18

30        351 parts of organopolysiloxane, containing  $\gamma$ -hydroxypropyl radical terminated  
with trimethylsilyl radical, and having an average molecular weight of 1404 and the  
general formula:



35 351 parts of toluene, 0.5 part of hydroquinone, 141 parts of methyl cinnamate ester, and 0.5 part of zinc acetate were placed in a three-necked flask, equipped with a fractionating column. The resulting mixture was kept at 110°C for 8 hours while reaction occurred, toluene was refluxed, and methanol was subjected to fractional distillation. When no more methanol was distilled, toluene and methyl cinnamate ester were removed by distillation under reduced pressure to obtain a pale yellow, transparent liquid photopolymerizable silicone compound having a viscosity of 108 cs (25°C), in a 96% yield (442 parts). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

40 40

	Photopolymerizable silicone prepared in the manner described above:	100 parts	
45	Azo green	4 parts	45
	n-propyl alcohol	50 parts	
	Toluene	50 parts	

After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical- and corrosion-resistance.

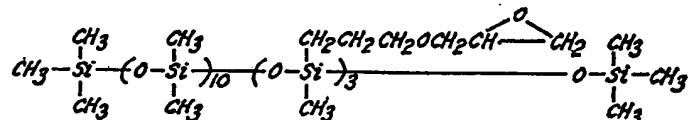
5

When picramide, 5-nitroacenaphthene, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyriliun perchlorate was used in place of the azo green, a similar result was obtained in each case.

10

## Example 19

142 parts of methylpolysiloxane, containing  $\gamma$ -glycidyloxypropyl radical terminated with trimethylsilyl radical, and having an average molecular weight of 1424 and the general formula:



15

0.5 part of hydroquinone, 150 parts of toluene and 1.0 part of anhydrous tin tetrachloride were placed in a three-necked flask and heated to 50°C. 29 parts of methacrylic acid was added dropwise, with stirring, over two hours and then stirring was continued at the same temperature for another 8 hours to allow reaction to occur. When the reaction ceased, toluene was removed from the reaction system by distillation under reduced pressure to obtain a pale yellow, transparent, liquid photopolymerizable silicone compound having a viscosity of 68 cs (25°C), in a 98% yield (164 parts).

15

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

25

Photopolymerizable silicone obtained  
in the manner described above:

100 parts  
4 parts  
100 parts

25

30

After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

30

35

When picramide, 5-nitroacenaphthene, or 4,4'-bis(dimethylamino)benzophenone, was used in place of the 2,4,6-triphenylpyriliun perchlorate, a similar result was obtained in each case.

35

## Example 20

40

237 parts of the siloxane used as starting material in Example 20, 0.5 part of hydroquinone, 300 parts of xylene and 1.0 part of anhydrous tin tetrachloride were placed in a three-necked flask, heated to 80°C, and 80 parts of 2-hydroxyethyl methacrylate was added dropwise with stirring, over three hours. Subsequently, the reaction system was stirred at the same temperature for a further 18 hours to allow reaction to occur. When the reaction ceased, xylene was removed by distillation under reduced pressure to obtain a pale yellow, transparent liquid photopolymerizable silicone compound having a viscosity of 95 cs (25°C), in a 95% yield (285 parts).

40

45

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

45

50

Photopolymerizable organopolysiloxane prepared  
in the manner described above:

100 parts  
4 parts  
100 parts

50

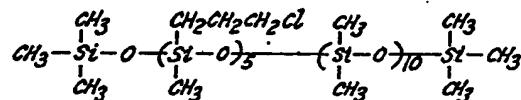
After this composition had been well stirred, it was spread, by means of a spinner, into a  $10 \mu$  thick layer over an aluminium plate, and was then exposed under reduced pressure to rays from a xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at  $150^\circ\text{C}$  to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

When picramide, methyl blue, 5-nitroacenaphthene, or 4,4'-bis(dimethylamino)benzophenone was used in place of the 2,4,6-triphenylthiapyriliun perchlorate, a similar result was obtained in each case.

10

## Example 21

317 parts of methylpolysiloxane, containing  $\gamma$ -chloropropyl radical, and having an average molecular weight of 1373 and the general formula:



15

was added dropwise, with stirring, over one hour to a mixture of 165 parts of cinnamic acid, 347 parts of toluene, 0.5 part of hydroquinone and 120 parts of triethylamine maintained at  $80-90^\circ\text{C}$ . The reaction system was allowed to react for a further 8 hours and was then cooled. Generated triethylamine hydrochloride was removed by filtration, and toluene and unreacted substances were removed by distillation under reduced pressure. A pale yellow, transparent liquid, photopolymerizable siloxane, having a viscosity of 50 cs ( $25^\circ\text{C}$ ) was obtained in a 98% yield (420 parts).

20

A photosensitizer and a solvent were added to this siloxane to give the following composition:

25

Photopolymerizable organopolysiloxane prepared in the manner described above:

2,4,6-triphenylpyriliun fluoroborate	100 parts
Toluene	4 parts
	100 parts

30

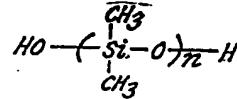
After this composition had been well stirred, it was spread, by means of a spinner, into a  $10 \mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried and heat-cured at  $150^\circ\text{C}$  to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

35

When picramide, methylene blue, 5-nitroacenaphthene or 4,4'-bis(dimethylamino)benzophenone was used in place of the 2,4,6-triphenylpyriliun fluoroborate, a similar result was obtained in each case.

40

247 parts of acryloxypropyltrichlorosilane was added dropwise over one hour to a mixture of 500 parts of water, 100 parts of toluene and 50 parts of isopropyl alcohol kept at  $5-10^\circ\text{C}$ , and after a hydrochloric acid layer had separated, the siloxane toluene layer was washed with water until its pH became 6.8. To the latter layer were added 612 parts of dihydroxydimethylsilicone, represented by the general formula:



45

(wherein  $n=10000$ ), 0.5 part of potassium acetate, and 0.5 part of hydroquinone, and the resulting mixture was reacted at  $110-115^\circ\text{C}$  for 8 hours. Subsequently, toluene was removed by distillation under reduced pressure to obtain a pale yellow, transparent, solid photopolymerizable silicone compound, having a pour point of  $45^\circ\text{C}$ , in a yield of 97% (754 part).

5

10

15

20

25

30

35

40

45

A photosensitizer and a solvent were added to this silicone compound to give the following composition.

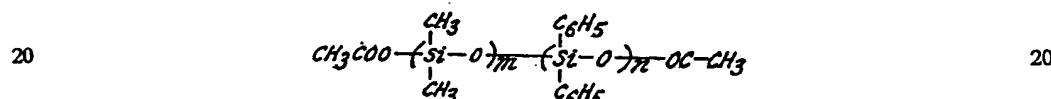
5	Photopolymerizable silicone prepared in the manner described above: 2,4,6-triphenylthiapyriliun fluoroborate Toluene	100 parts 4 parts 1000 parts	5
---	---	------------------------------------	---

After this composition had been well stirred, it was spread, by means of a spinner, into a  $10 \mu$  thick layer over an aluminium plate and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

When picramide, 5-nitroacenaphthene, or 4,4'-bis(dimethylamino)benzophenone was used in place of the 2,4,6-triphenylthiapyriliun fluoroborate, a similar result was obtained in each case.

#### Example 23

To 92 parts of the siloxane (65% toluene concentration) used as starting material in Example 23 were added 276 parts of diacetoxymethylphenylsiloxane, represented by the general formula:



(where  $m+n=5000$ , and  $n/(m+n)=0.05$ ), 0.5 part of potassium acetate, and 0.5 part of hydroquinone, and the resulting mixture was reacted in the manner described in Example 23 for 10 hours, while generated acetic acid was removed. A colourless, transparent solid photopolymerizable silicone compound having a pour point of 53°C was obtained in a yield of 98% (361 parts).

25 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

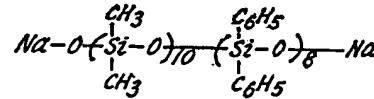
30	Photopolymerizable silicone prepared in the manner described above: 4,4'-bis(dimethylamino)benzophenone Toluene	100 parts 4 parts 1000 parts	30
----	--	------------------------------------	----

After this composition had been well stirred, it was spread, by means of a spinner, into a  $10 \mu$  thick layer over an aluminium plate, and was then exposed to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

When picramide, methylene blue, or 2,4,6-triphenylpyriliun perchlorate was used in place of the 4,4'-bis(dimethylamino)benzophenone, a similar result was obtained in each case.

#### Example 24

239 parts of disodium methylphenyl siliconate, having an average molecular weight of 2386 and the general formula:



45 and 239 parts of toluene were placed in a four-necked flask, and, while the resulting mixture was stirred at room temperature, 28 parts of  $\gamma$ -methacryloxypropyltrichloro-

5 silane was added dropwise over one hour. Subsequently, stirring was continued for 8 hours to allow reaction to occur. When the reaction ceased, the reaction product was washed with water until its pH became 7.0, and toluene was removed by distillation under reduced pressure. A photopolymerizable silicone compound having a pour point of 80°C was obtained in a 96% yield (251 parts).

5

A photosensitizer and a solvent were added to this silicone compound to give the following composition:

	Photopolymerizable silicone prepared in the manner described above:	100 parts	
10	5-nitroacenaphthene	4 parts	10
	Toluene	1000 parts	

15 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a super-high pressure 800 W mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried and heat-cured at 150°C to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance. When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyrilium perchlorate was used in place of the 5-nitroacenaphthene, a similar result was obtained in each case.

15

20 Example 25

20 149 parts of monomethyltrichlorosilane, 280 parts of  $\gamma$ -methacryloxypropyltrichlorosilane, and 258 parts of diphenyldichlorosilane were placed in a four-necked flask, and 224 parts of methanol was added over one hour with stirring. Subsequently, the resulting mixture was heated to 98°C, while attention was paid to the generation of hydrochloric acid, and then the temperature was lowered to 50°C or under. Next, 1.5 parts of ferric chloride was added and the reaction system was gradually heated, while attention was paid to the generation of methyl chloride, so that reaction was carried out at 120°C for 5 hours. When no more methyl chloride was generated, 792 parts of toluene was added to the reaction product, which was then washed with water until its pH became 7.0. Toluene was then removed from the reaction product by distillation under reduced pressure to obtain a solid photopolymerizable silicone compound having a pour point of 95°C, in a 95% yield (755 parts).

20

25 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

35	Photopolymerizable silicone prepared in the manner described above:	100 parts	35
	4,4'-bis(dimethylamino)benzophenone	4 parts	
	Toluene	1000 parts	

40 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

40

45 When 5-nitroacenaphthene, or 2,4,6-triphenylpyrilium perchlorate was used in place of the 4,4'-bis(dimethylamino)benzophenone, a similar result was obtained in each case.

45

#### Example 26

50 115 parts of methylhydrogen dichlorosilane, 149 parts of monomethyltrichlorosilane, 211 parts of monophenyltrichlorosilane and 516 parts of dimethyldichlorosilane were added dropwise over two hours to a mixture of 1000 parts of toluene, 100 parts of methanol and 5000 parts of water, stirred and maintained at 5-10°C. The resulting mixture was washed with water until its pH became 7.0 and then toluene was removed by distillation under reduced pressure until the siloxane concentration of the reaction mixture reached 50%. Subsequently, a mixture of 138 parts of allyl methacrylate, 0.2 part of a 2% isopropanol solution of chloroplatinic acid and 0.5 parts of hydroquinone was slowly added dropwise to the system, while attention was paid to the generation of heat. When the addition was over, the resulting mixture was heated to 80°C, and then allowed to react at this temperature for 10 hours. When the reaction

50

55

ceased, unreacted substances and toluene were removed by distillation under reduced pressure to obtain a solid photopolymerizable silicone compound having a pour point of 48°C, in a yield of 95% (628 parts).

5 A photosensitizer and a solvent were added to this silicone compound to give the following composition:

5

Photopolymerizable silicone prepared  
in the manner described above:  
Picramide 100 parts  
Toluene 4 parts  
1000 parts

10 After this composition had been well stirred, it was spread, by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate, and was then exposed, under reduced pressure, to rays from an 800 W super-high pressure mercury arc lamp, placed 40 cm away, for 1-2 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance. When 5-nitroacenaphthene, methylene blue, 15 4,4'-bis(dimethylamino)benzophenone, or 2,4,6-triphenylpyrilium perchlorate was used in place of the picramide, a similar result was obtained in each case.

10

20 Example 27  
A mixture of 198 parts of  $\gamma$ -chloropropyl trimethoxysilane, and 91 parts of  $\gamma$ -chloropropyl methyldichlorosilane was added dropwise over one hour to a mixture of 200 parts of toluene, 500 parts of water and 50 parts of isopropyl alcohol, stirred at 5-10°C. The resulting mixture system was washed with water until its pH became 7.0 so that a siloxane layer separated. 162 parts of sodium cinnamate was added to this layer at room temperature, and the resulting mixture was reacted at 80°C for 5 hours. Unreacted substances and sodium chloride and other byproducts were removed by filtration, and toluene was removed by distillation under reduced pressure to obtain 320 parts of a pale yellow, transparent solid photopolymerizable silicone compound having a pour point of 95°C. A photosensitizer and a solvent were added to this silicone compound to give the following composition:

20

25 30 Photopolymerizable silicone prepared  
in the manner described above:  
4,4'-bis(dimethylamino)benzophenone 100 parts  
Toluene 4 parts  
1000 parts

25

35 After this composition had been well stirred, it was spread by means of a spinner, into a 10  $\mu$  thick layer over an aluminium plate and was then exposed, under reduced pressure, to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at 150°C to produce a strong, insoluble and hard film having superior heat-, chemical-, and corrosion-resistance.

35

40 When 5-nitroacenaphthene, picramide, methylene blue or 2,4,6-triphenylpyrilium perchlorate was used in place of the 4,4'-bis(dimethylamino)benzophenone, a similar result was obtained in each case.

40

45 Example 28  
415 parts of a toluene solution of the siloxane used as starting material in Example 27 was added dropwise over one hour to a mixture of 285 parts of glycidyl acrylate, 0.5 part of a 2% butanol solution of chloroplatinic acid, and 0.5 part of hydroquinone kept at 80°C, and the resulting mixture was allowed to react for a further 8 hours. After the reaction ceased, the reaction system was cooled to 50°C, 375 parts of cinnamic acid and 2.5 parts of tin tetrachloride were added and the system was kept at the same temperature for a further 10 hours. When the reaction ceased, unreacted substances and toluene were removed by distillation under reduced pressure to obtain 50 a solid photopolymerizable silicone compound having a pour point of 60°C, in a yield of 93% (999 parts). A photosensitizer and a solvent were added to this silicone compound to give the following composition:

45

55 55 Photopolymerizable silicone obtained  
in the manner described above:  
5-nitroacenaphthene 100 parts  
Toluene 4 parts  
1000 parts

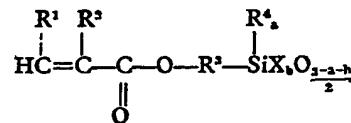
50

After this composition had been well stirred, it was spread, by means of a spinner, into a  $10 \mu$  thick layer over an aluminium plate, and was then exposed to rays from a 3000 W xenon lamp, placed 50 cm away, for 3-4 minutes. The layer was then developed with methyl ethyl ketone, dried, and heat-cured at  $150^\circ\text{C}$  to produce a strong, insoluble and hard film, having superior heat-, chemical-, and corrosion-resistance.

When picramide, methylene blue, 4,4'-bis(dimethylamino)benzophenone or 2,4,6-triphenylpyrrilium perchlorate was used in place of the 5-nitroacenaphthene, a similar result was obtained in each case.

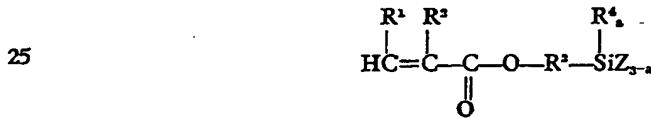
10 WHAT WE CLAIM IS:—

1. A photopolymerizable composition comprising (1) at least one organopolysiloxane containing at least one photopolymerizable organosilicon unit of the general formula:

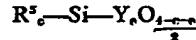


15 where  $\text{R}^1$  is a hydrogen atom or an unsubstituted or halogen-substituted phenyl radical,  $\text{R}^2$  is a hydrogen atom or a methyl radical,  $\text{R}^3$  is an unsubstituted or halogen-substituted bivalent  $\text{C}_{1-10}$  hydrocarbon radical optionally interrupted by an ether and/or ester linkage,  $\text{R}^4$  is an unsubstituted or halogen-substituted univalent  $\text{C}_{1-10}$  hydrocarbon radical,  $\text{X}$  is a hydroxy or  $\text{C}_{1-4}$  alkoxy radical, and  $a$  is 0 or 1, and  $b$  is 0, 1 or 2, with the proviso that  $(a+b)=0, 1$  or  $2$ .

20 2. A photopolymerizable composition as claimed in claim 1, in which said organopolysiloxane is prepared by condensation of a photopolymerizable organic silicon monomer of the general formula:

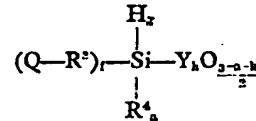


where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\alpha$  are as defined in claim 1 and  $Z$  is a halogen atom or an acetoxy, hydroxy or  $\text{C}_{1-4}$  alkoxy radical, with a silane or siloxane comprising at least one unit of the general formula:



30 where  $\text{R}^5$  is an unsubstituted or halogen-substituted univalent  $\text{C}_{1-10}$  hydrocarbon radical,  $\text{Y}$  is a halogen atom or an acetoxy, hydroxy,  $\text{NaO}$ — or  $\text{C}_{1-4}$  alkoxy radical,  $c$  is 0, 1, 2 or 3 and  $e$  is 1, 2, 3 or 4, with the proviso that  $(c+e)$  is not greater than 4.

35 3. A photopolymerizable composition as claimed in claim 1, in which said organopolysiloxane is prepared by first subjecting a silane or siloxane comprising at least one unit of the general formula:



40 where  $\text{R}^2$ ,  $\text{R}^4$  and  $\alpha$  are as defined in claim 1,  $\text{Y}$  is as defined in claim 2,  $\text{Q}$  is a halogen atom or a hydroxy or epoxy group,  $h$  is 0, 1, 2 or 3 and  $f$  and  $g$  are each 0 or 1 with the proviso that  $(f+g)=1$  and that  $(a+h)$  is not greater than 3, to a condensation reaction with a silane or siloxane comprising at least one unit of the general formula:

5

10

15

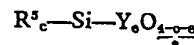
20

25

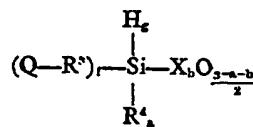
30

35

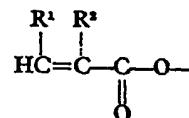
40



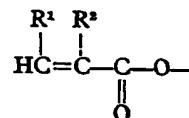
where  $R^5$ ,  $Y$ ,  $c$ ,  $e$  and  $(c+e)$  are as defined in claim 2, to produce an organopolysiloxane containing at least one unit of the general formula:



5 where  $Q$ ,  $f$ ,  $g$  and  $(f+g)$  are as defined above and  $R^5$ ,  $R^4$ ,  $X$ ,  $a$ ,  $b$  and  $(a+b)$  are as defined in claim 1, and then reacting the organopolysiloxane thus obtained with an organic compound which contains a photopolymerizable organic radical of the general formula:



10 and an aliphatic unsaturated bond in the case where  $f=0$  or is an alkali metal or tertiary amine salt of a carboxylic acid containing a photopolymerizable organic radical of the general formula:



15 in the case where  $f=1$ ,  $R^1$  and  $R^2$  being as defined in claim 1.

4. A photopolymerizable composition as claimed in any preceding claim containing from 0.05% to 5.0% by weight of component (2) with respect to component (1).

5. A photopolymerizable composition as claimed in any preceding claim also comprising a thermal polymerization inhibitor.

6. A photopolymerizable composition as claimed in any preceding claim also comprising a filler.

7. A photopolymerizable composition as claimed in any preceding claim also comprising a diluent as hereinbefore defined.

8. A photopolymerizable composition, substantially as hereinbefore described in any one of the Examples.

For the Applicants,  
D. YOUNG & CO.,  
Chartered Patent Agents,  
9 & 10 Staple Inn,  
London WC1V 7RD.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.